

Polarization of infrared-active in-plane modes in a monoclinic molecular crystal

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Abstract—The absorption of eleven in-plane (B_u') modes of monoclinic adipic acid [$\text{HOOC}(\text{CH}_2)_4\text{COOH}$] was investigated as a function of the angle between the electric vector of the radiation beam and the crystallographic c -axis in order to obtain information concerning the interrelationship between frequency-dependent dielectric axes, directions of transition moment vectors, and chemical structure in a molecular crystal with low symmetry. Some approximations which have been used in the past to interpret absorption spectra obtained with polarized infrared radiation are briefly evaluated and the applicability of the results to some related systems is discussed.

It is frequently assumed that in molecular crystals (and oriented high polymers) the directions of vibrational transition moment vectors may be found by applying a relationship of the form

$$A \propto |\mathbf{P} \cdot \mathbf{E}|^2 \cos^2 \alpha \quad (1)$$

to absorption data obtained with linearly polarized infrared radiation [1–12]. A is absorbance, \mathbf{P} the transition moment vector, \mathbf{E} the electric vector of the radiation beam and α the angle between the two vectors. The results thus obtained are sometimes used to estimate structural parameters on the assumption that the direction of \mathbf{P} coincides approximately with the direction of the chemical bond which is primarily involved [2, 3, 4, 6], even in cases where neither direction is determined by the symmetry of the sample. An equation of the form: $R = 2 \cot^2 \beta$, which implies that $R = 1$ if $\beta = 54^\circ 44'$, has been used to correlate infrared dichroism and structure in uniaxially oriented high polymers [6, 7, 8, 9]. Here R is the dichroic ratio and β is the angle between the transition moment vector and the main axis of the polymer chain.

A real anisotropic and absorbing crystal acts in general itself as a dichroic polarizer, resolving linearly polarized incident radiation into two waves with different velocities and amplitudes, whereby the two waves are absorbed differently

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- [1] G. R. WILKINSON, W. C. PRICE and E. M. BRADBURY, *Spectrochim. Acta* **14**, 284 (1959).
 - [2] E. J. AMBROSE, A. ELLIOTT, R. B. TEMPLE, *Proc. Roy. Soc. A* **206**, 192 (1951).
 - [3] E. J. AMBROSE and A. ELLIOTT, *Proc. Roy. Soc. A* **206**, 206 (1951).
 - [4] E. J. AMBROSE, A. ELLIOTT and R. B. TEMPLE, *Proc. Roy. Soc. A* **199**, 183 (1949).
 - [5] C. Y. LIANG and S. KRIMM, *J. Chem. Phys.* **27**, 327 (1957).
 - [6] C. Y. LIANG and S. KRIMM, *J. Chem. Phys.* **27**, 1437 (1957).
 - [7] R. D. B. FRASER, *J. Chem. Phys.* **21**, 1511 (1953).
 - [8] R. D. B. FRASER, *J. Chem. Phys.* **28**, 1113 (1958).
 - [9] R. D. B. FRASER, *J. Chem. Phys.* **29**, 1428 (1958).
 - [10] M. BEER, *Proc. Roy. Soc. A* **236**, 136 (1956).
 - [11] R. M. HEXTER and H. CHEUNG, *J. Chem. Phys.* **24**, 1186 (1956).
 - [12] R. M. HEXTER and D. A. DOWS, *J. Chem. Phys.* **25**, 504 (1956).

[13, 14]. WARD [15] has presented a detailed discussion of absorbing crystals in connexion with measurements on ultra-violet dichroism. The treatment, which is based on electro-magnetic theory, is of general validity and particularly convenient to use in connexion with problems of molecular spectroscopy. It differs from earlier treatments in that it uses real co-ordinates which coincide with the eigenvectors of the dielectric tensor.

The medium is considered to be non-magnetic and its electrical properties are assumed to be given by the equations

$$D_i = \sum_j \epsilon_{ij} E_j \quad (2)$$

$$-\dot{\omega} = \sum_{ij} \sigma_{ij} E_i E_j \quad (3)$$

where $\sigma_{ij} = \sigma \sum_k L_{ik} L_{jk}$

The ϵ_{ij} are the components of the dielectric constant tensor, $-\dot{\omega}$ is the rate of dissipation of electrical energy, the σ_{ij} correspond formally to the components of the conductivity tensor, L_{ik} are the direction cosines of the k -th transition moment in the unit cell, D and E have their usual meanings [13]. The constant σ depends only on the absolute absorption intensity and cancels out when dichroic ratios are calculated. For linearly polarized perpendicularly incident radiation propagated along the b axis of a monoclinic crystal the following relations are obtained [15]:

$$I_\theta = \frac{E_0^2}{8\pi} \left[\exp(-k_y d) \cos^2 \theta + \exp(-k_x d) \sin^2 \theta \right] \quad (4)$$

$$k_y = \frac{4\pi\sigma \cos^2 \phi}{c\epsilon_y^{1/2}} \quad k_x = \frac{4\pi\sigma \sin^2 \phi}{c\epsilon_x^{1/2}} \quad (5)$$

$$R = \frac{k_y}{k_x} = \left(\frac{\epsilon_x}{\epsilon_y} \right)^{1/2} \cot^2 \phi \quad (6)$$

I_θ is the intensity of the emerging radiation, k_y and k_x are absorption coefficients along the in-plane principal axes of the dielectric ellipsoid, d is the thickness of the sample, R the dichroic ratio in terms of k_y and k_x , θ the angle between the electric vector and the y direction, ϕ the angle between the transition moment vector and the y direction, ϵ_x and ϵ_y dielectric constants along x and y . Equation (4) can be rewritten in the slightly different form:

$$A_\theta = -\log T = -\log (T_y \cos^2 \theta + T_x \sin^2 \theta) \quad (4a)$$

where A_θ is observed absorbance, T_y and T_x are the principal transmittances. The graphical relationship of various parameters to each other and to the ac -plane of

[13] M. BORN and E. WOLF, *Principles of Optics*, Pergamon Press, London (1959).

[14] C. D. WEST and R. C. JONES, *J. Opt. Soc. Amer.* **41**, 976 (1951).

[15] J. C. WARD, *Proc. Roy. Soc. A* **228**, 205 (1955).

monoclinic adipic acid is illustrated in Fig. 1. The directions of y , x and \mathbf{P} are, of course, frequency dependent. Equations (4), (5) and (6) are obtained from general equations for the complex dielectric index—which follow rigorously from the relations (2) and (3)—by neglecting higher order terms of σ . Differentiation of equation (4) with respect to θ yields maxima or minima at $\theta = 0, 1/2\pi, \pi, 3/2\pi, 2\pi \dots$. Thus, the orientation of the dielectric ellipsoid is found by applying equation (4a). The orientation of \mathbf{P} with respect to the in-plane dielectric axes is given by equation (6).

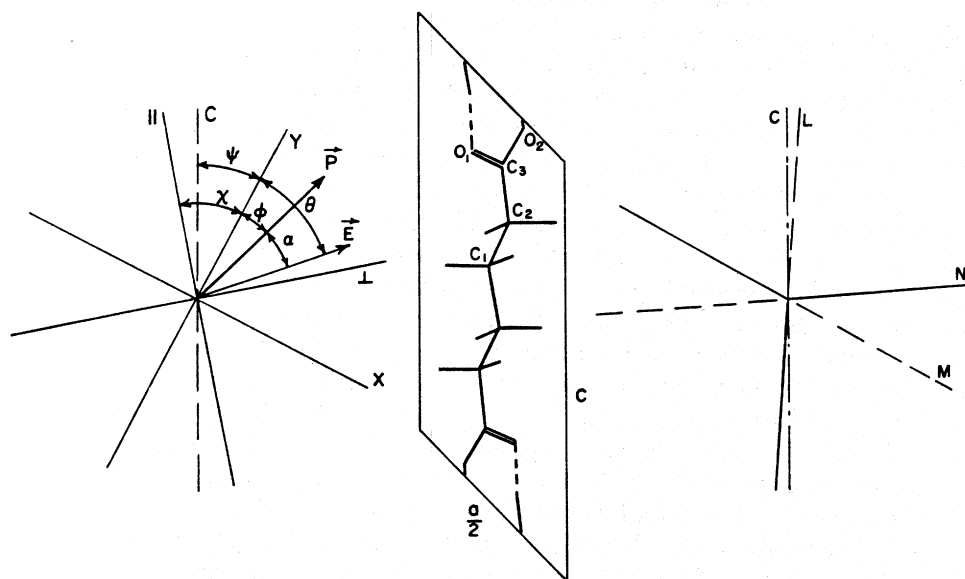


Fig. 1. Schematic structure and coordinate system. a, c , crystallographic axes; x, y , dielectric axes; II, L , axes of prism polarization; \mathbf{P} , transition moment vector; \mathbf{E} , electric vector of the radiation beam; L, M, N , molecular axes. All angles clock-wise.

Some consequences of equations (4), (5) and (6) do not appear to have always received proper consideration:

- (a) Maximum and minimum absorption does not necessarily coincide with the polarizer position parallel or perpendicular to the vibrating dipole;
- (b) Absorption is in general not proportional to the square of the dot product of the electric vector and the transition moment vector, as stated by equation (1);
- (c) Equation (6) contains a term ϵ_x/ϵ_y . These statements have general validity, although cited here in connexion with a special case.

Analysis of polarization data is considerably simplified if the transition moment vectors and the orientation of the dielectric ellipsoid are both symmetry fixed [16]. Unfortunately, this is an exceptional case for crystals of larger molecules. The purpose of the present study is to investigate the dependence of absorption upon

[16] R. NEWMAN and R. S. HALFORD, *J. Chem. Phys.* **18**, 1276 (1950).

the direction of the electric vector of the beam in a case where the orientation of the dielectric ellipsoid and of the transition moment vectors is not symmetry fixed; to estimate the directions of the transition moment vectors and the dielectric axes, and to gain some empirical information concerning the relationship between the transition moment vectors and the directions of chemical bonds in a crystal where reasonable assignments are available. An assignment of the infrared active fundamentals of crystalline adipic acid was reported previously [17].

Sample and techniques

The space group of crystalline adipic acid is $C_{2h}^5 - P2_{1/a}$ [18]. In the factor group approximation [19, 20] each observable infrared active fundamental is split into an A_u' branch with the transition vector parallel to the crystallographic b -axis and a B_u' branch with the transition vector within the ac -plane. A_u' and B_u' refer to factor-group symmetry. If perpendicularly incident radiation is propagated along the b -axis, A_u' branches become inactive and one obtains a system corresponding to a two-dimensional model where the dielectric axes and transition moments are confined to the ac -plane, but are not otherwise symmetry fixed. Such a system is considerably easier to investigate experimentally than the more general triclinic case, but should in principle exhibit similar phenomena.

The sample was prepared by a previously described method [17]. It consisted of a thin crystal layer between two rock-salt plates, the crystallographic b -axis being perpendicular to the sample plane. Fig. 2 shows a photograph of the specimen between rock-salt plates. No A_u' branches [17] could be observed with perpendicular incidence. Twinning along the c - or a -axis could produce misleading results and still leave the A_u' branches inactive, but this possibility seems unlikely in view of Fig. 2 and the experimental results. Investigation with a polarizing microscope also indicated a uniform sample. The sample, which had an area of about 1.5×10 mm, was mounted next to the entrance slit of a Perkin-Elmer Model 21* instrument equipped with a sodium-chloride prism and a six-plate silver-chloride polarizer. Spectra from 4000 to 600 cm^{-1} were obtained with polarizer orientations 10° apart. The 736 cm^{-1} CH_2 rocking band was in addition studied on a specimen which was large enough to permit rotation of the sample about the axis perpendicular to the sample surface (b -axis), but was too thick for measurements on most absorption bands. No correction was made for polarizer imperfection. The observed data indicate (Fig. 3, 4) that the error hereby introduced was not very large, a number of medium to strong bands exhibiting no detectable absorption with the polarizer perpendicular to the direction of maximum absorption. Polarizer imperfection could change the absolute intensities, but would not influence positions of maxima or minima. The effect of beam convergence is small, if no beam condensing device is used. A qualitative check is furnished by the absence of A_u' branches [17]. Errors caused by reflexion are difficult to estimate. If the (real)

* Mention of commercial products does not constitute an endorsement of the U.S. Department of Agriculture over others of a similar nature not mentioned.

[17] H. SUSI, *Spectrochim. Acta* **15**, 1063 (1959).

[18] J. D. MORRISON and J. M. ROBERTSON, *J. Chem. Soc.* 987 (1949).

[19] D. F. HORNIG, *J. Chem. Phys.* **16**, 1063 (1948).

[20] H. WINSTON and R. S. HALFORD, *J. Chem. Phys.* **17**, 807 (1949).

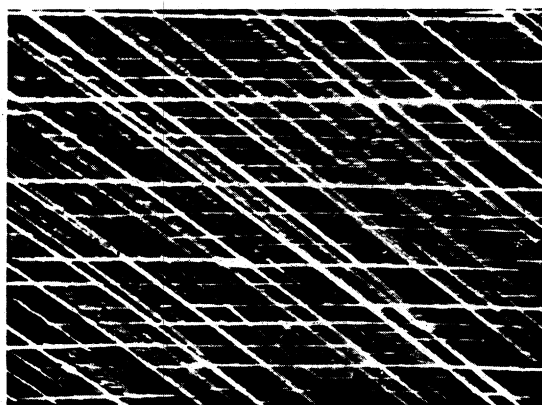


Fig. 2. Crystalline sample between rock-salt plates. The horizontal lines are parallel to the c -axis ($50\times$ magnification)

refractive index in the vicinity of an absorption band i is treated as a sum $\{\bar{n} + n(\nu_i)\}$ [21], (\bar{n} is independent of frequency) the errors caused by \bar{n} can be approximately eliminated by the base line method (see below). $n(\nu_i)$ changes the shape of the observed band, resulting in a dispersion curve superimposed on an absorption curve (Christiansen Effect). Most observed bands were approximately symmetrical, two exceptions being noted later.

Instrument polarization deserves a few remarks. The sodium-chloride prism acts as a polarizer with $T_{\perp}/T_{\parallel} \approx 0.8$, where T_{\parallel} and T_{\perp} are transmittance values for radiation with the electric vector parallel and perpendicular to the prism base [22, 23]. The sample thus constitutes an anisotropic crystal plate mounted between two polarizers, with the result that parts of the x and y beams emerging from the sample (which stem from the same monochromatic, linearly polarized original beam) are brought to interference. The intensity obtained from the interference of two monochromatic waves with phase difference δ is given by $I = I_1 + I_2 + 2\sqrt{I_1 I_2} \cos \delta$ [13]. Unless the x or y direction (Fig. 1) coincides with the direction of the prism base, a $-\log T$ vs. $(\psi + \theta)$ curve results which is not symmetrical about T_{\max} as required by equation (4). Interference depends on δ and thus on the wavelength, sample thickness and the two principal real in-plane refractive indices [13]. The latter three quantities could not be estimated with any degree of reliability. The qualitative effect of instrument polarization on data obtained on the 736 cm^{-1} band is shown in Fig. 3.

Transmittance values were measured relative to a base line estimated as well as possible for each absorption band. Reference points for estimating I_0 were chosen at frequencies of maximum transmittance on either side of the absorption band. This method, while admittedly involving some uncertainties, probably leads to least objectionable results for complex systems where many bands overlap. It also tends to minimize errors caused by reflection and scattering.

Results

A survey spectrum and assignments have been reported previously [17]. Fig. 3(a) shows the absorption of the B_u' branch of the 736 cm^{-1} CH_2 rocking fundamental as a function of the polarizer angle $(\psi + \theta)$ (cf. Fig. 1). The 736 cm^{-1} fundamental is one of the few bands relatively free from overlap and therefore suited for a more detailed study. The experimental points in Fig. 3(a) were obtained with the sample mounted in such a way that maximum absorption was observed with **E** parallel to the entrance slit. The observation that A_{\min} is zero (within instrumental error) indicates that for this band the direction of the transition moment vector is very close to one of the principal dielectric axes and is therefore given by the direction of maximum absorption. The continuous line in Fig. 3(a) was calculated by equation (4a) (taking A_{\max} as reference), the dotted line by equation (1). It is evident that equation (1) constitutes a poor approximation and might lead to serious errors. In the present example $(A/A')_{\theta=45^\circ} \simeq 0.5$, if A' is

[21] H. PRIMAS and H. H. GÜNTARD, *Helv. Chim. Acta* **37**, 360 (1954).

[22] E. CHARNEY, *J. Opt. Soc. Amer.* **45**, 980 (1955).

[23] A. S. MAKAS and W. A. SHURCLIFF, *J. Opt. Soc. Amer.* **45**, 998 (1955).

the value calculated by equation (1). It is probably worth mentioning that very similar results would in principle be obtained for *uniaxial systems*, if linearly polarized radiation is propagated normal to the optic axis. (For propagation parallel to the optic axes no polarization would be observed.) Again, the incident radiation is resolved into two waves and—to the approximation that has been

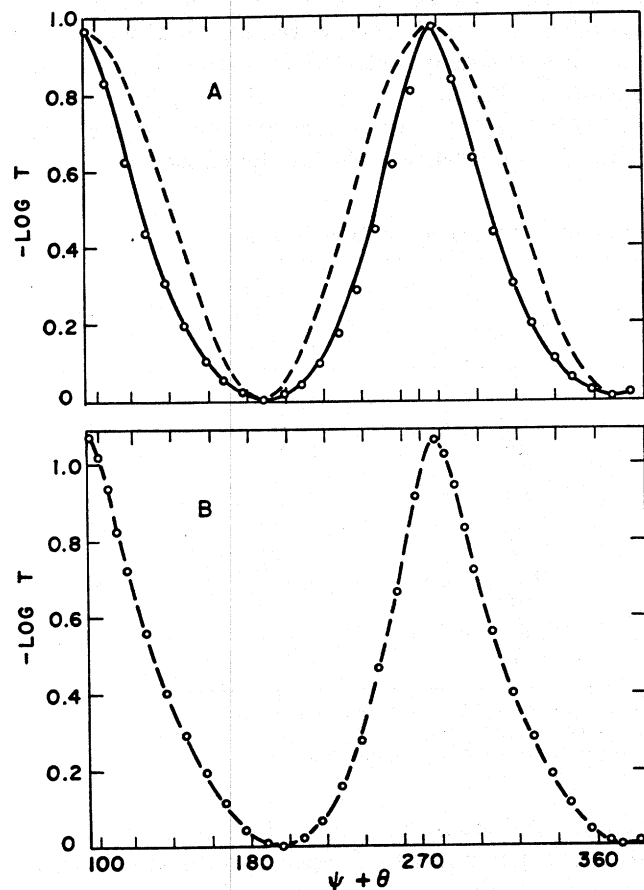


Fig. 3. Absorbance of the 736 cm^{-1} fundamental as a function of polarizer angle. (A) $\chi = 0$; dotted line calculated by equation (1), solid line calculated by equation (4A). (B) $\chi = 41^\circ$.

used [15]—apparent absorbance is given by a relation similar to equation (4a). For a parallel band (**P** parallel to the optic axis):

$$A_\theta = -\log T = -\log [T_{\parallel} \cos^2 \theta + (1) \sin^2 \theta]$$

$$\therefore A_\theta \neq \text{const.} \cos^2 \theta$$

Similarly, for a perpendicular band:

$$A_\theta = -\log T = -\log [(1) \cos^2 \theta + T_{\perp} \sin^2 \theta]$$

Here θ is the angle between **E** and the optic axis. If unresolved parallel and

perpendicular components are present [6-8], then for truly uniaxial systems $R = 2 \cot^2 \beta$ (β corresponds to α in Refs. 6-8) still holds, because only measurements with $\theta = 0, 1/2\pi, \pi \dots$ are involved.

The effect of interference caused by instrument polarization is illustrated in Fig. 3(b). Absorption at 736 cm^{-1} was measured as a function of the polarizer angle with $\chi = 41^\circ$ (cf. Fig. 1). Analogous results concerning the form of the $-\log T$ vs. $(\psi + \theta)$ curves and the effect of interference were also obtained on the second mode which was suitable for sufficiently detailed investigation, the B_u' branch of the 687 cm^{-1} COO deformation band.

The remaining bands were either too intense or overlapped too strongly for quite as detailed measurements, but the general features of the observed $-\log T$

Table 1. Polarization of B_u' branches of fundamentals

cm^{-1}	Assignment	ψ^* (degrees)	$\phi' \equiv \arccot \left(\frac{k_y}{k_x} \right)^{1/2 \dagger}$ (degrees)	$\Omega \ddagger$ (degrees)
3000	OH st.	5	(± 8)	8
1695	C=O st.	68	± 35	115
1463	CH ₂ b.	26	$< \pm 5$	120
1433	CO st. (OH b.)	171	(± 8)	
1408	CH ₂ b.	95	$< \pm 5$	120
1357	CH ₂ wag.	155	(± 12)	184
1287	OH b. (CO st.)	158	(± 23)	
1200	C ₃ C ₂ st.	150	± 16	176
932	OH out-of-plane b.	91	$< \pm 5$	87
736	CH ₂ rock.	98	$< \pm 5$	87
687	COO def.	8	$< \pm 5$	

* Cf. Fig. 1. Axis of maximum absorption taken as y at any given frequency.

\dagger Angle between y and \mathbf{P} , if (ϵ_x/ϵ_y) in equation (6) is assumed to be unity.

\ddagger Angle between ideal, hypothetical, transition moment vector and c -axis.

vs. $(\psi + \theta)$ curves of ten additional fundamentals, shown in Fig. 4, appeared sufficiently recognizable to permit some conclusions. Pertinent data are listed in Table 1. The values of ψ should be correct within $\pm 3^\circ$ or better. The values of ϕ' , which correspond to ϕ (cf. Fig. 1 and equation 6) if (ϵ_x/ϵ_y) in equation (6) is assumed to be unity, are subject to greater uncertainty because measurements of (k_y/k_x) are influenced by the spectral slit width, by polarizer imperfections, and are sensitive to the chosen base line. If k_y or k_x is small, ϕ' becomes a very sensitive function of the observed parameters T_y and T_x , a 1 per cent error in the reading of maximum transmittance leading to errors in ϕ' of the order of 5 degrees. The sign of ϕ' cannot be determined unambiguously from equation (6), although in some instances a positive or negative value is more probable in view of the known structure. The angles Ω , giving the projections of the transition moment directions of hypothetical, totally separable group vibrations on the ac -plane were calculated from data in Ref. [18], the hypothetical pure CH₂ modes being taken to be polarized parallel to one of the principal molecular axes L, M, N . (L is defined by the

mid-points of CC bonds; M is perpendicular to L and within the plane of the carbon skeleton; N is perpendicular to M and L [18]). The $\widehat{\text{COH}}$ angle (not given in available crystallographic data) was assumed to be 105° .

The directions of the transition moment vectors of five bands (CH_2 bend.

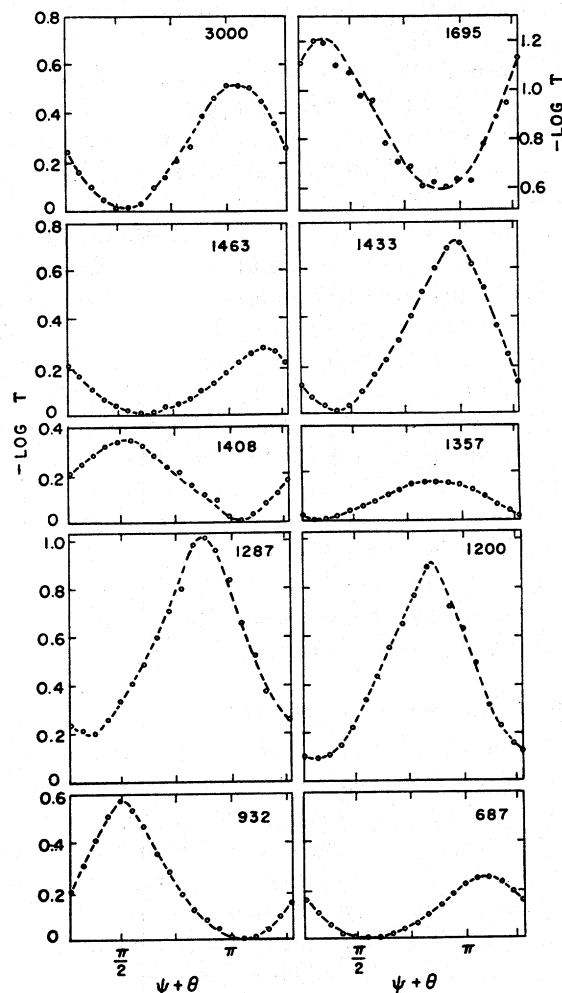


Fig. 4. Absorbance of ten B_u' branches of fundamental modes as a function of the polarizer angle. The numbers in the upper right-hand corners are frequencies in cm^{-1} .

1463 cm^{-1} , CH_2 bend. 1408 cm^{-1} , OH bend. 932 cm^{-1} , CH_2 rock. 736 cm^{-1} , COO def. 687 cm^{-1}) appear to coincide within experimental error with one of the principal dielectric axes, and thus with the direction of \mathbf{E} for maximum absorption. For these bands the direction of the transition moment can thus be estimated relatively accurately, even though it is not determined by symmetry. For two bands ($\text{C}=\text{O}$ str. 1695 cm^{-1} and C_2C_3 str. 1200 cm^{-1}), on the other hand, the direction of \mathbf{E} for maximum absorption must differ considerably from the direction

of the transition moment vector, ϕ' being approximately $\pm 35^\circ$ and $\pm 16^\circ$, respectively. These two bands also showed a clearly recognizable Christiansen Effect, which appeared to depend on the polarizer angle, as expected. For the remaining bands the ϕ' values are more uncertain because of extreme broadness of the bands, overlap, or both. These ϕ' values are given in parenthesis in Table 1. The data observed on the OH stretching band agree within experimental error with previous measurements by other investigators [2].

Eight of the investigated bands (OH str.; C=O str., two CH₂ b., CH₂ wag., C₂C₃ str., OH out of plane b., CH₂ rock.) can be approximately described as separable group vibrations for which an ideal (hypothetical) transition moment direction could be postulated on the grounds of bond directions and local symmetry. For five of these bands (OH str., C=O str., C₃C₂ str., OH o.o.p. b., CH₂ rock.) including two with relatively large ϕ' (C=O str., C₃C₂ str.), the estimated transition moment direction comes to within $\pm 12^\circ$ of the ideal, hypothetical, value if a proper sign is chosen for ϕ' . For the other three bands, the deviations are considerable. The weak 1357 cm⁻¹ CH₂ wagging mode can be dismissed because the measured ϕ' value is very approximate, but for the two CH₂ bending modes at 1463 and 1408 cm⁻¹, ϕ' appears to be very small and the direction of the transition moment vector correct certainly within ± 10 degrees. The deviation from the "ideal" direction is about 95° for one band and 25° for the other. The assignment of these bands is based on comparison with a very large number of related molecules [24] and on deuteration studies [17], and seems, therefore, to be correct.

ψ and ϕ' values could not be evaluated for the B_u' branches of CH₂ stretching fundamentals because of strong interference by the very intense OH stretching band. Purely qualitatively, the ϕ' values seemed to be small and the ψ values to lie in the vicinity of 90° , close to the ideal directions.

Discussion and conclusions

Of the B_u' branches of fundamentals which could be studied with some accuracy two exhibited a relatively large ϕ' value. This points to the necessity of studying well oriented samples and discarding the simple dot-product approximation [equation (1)] before any conclusions can be reached concerning the directions of transition moment vectors in systems of low symmetry. Otherwise there appears to be no way to determine to what extent observed dichroic ratios (A_{\max}/A_{\min}) are influenced by sample randomness and to what extent by deviations of transition moment vectors from the principal axes of the dielectric ellipsoid. In well oriented systems an uncertainty still remains because it is difficult to determine the principal dielectric constants (ϵ_y and ϵ_x in equation 6) at frequencies close to the centers of absorption bands. The observation that for many bands ϕ' was close to zero indicates that the transition moment directions of some fundamentals can be evaluated with reasonable accuracy even in systems with low symmetry, provided the sample is sufficiently well oriented to establish that ϕ is indeed small (a value of $A_{\max}/A_{\min} = 130$, corresponding to $\phi' \simeq \pm 5^\circ$, constitutes an approximate instrumental limit for conventional prism spectrometers).

[24] L. J. BELLAMY, *The Infra-red Spectra of Complex Molecules*. John Wiley, New York (1958).

The same considerations should apply to oriented biaxial polymers with lower than orthorhombic symmetry. "Uniaxially oriented" biaxial polymers (such as some cellulose fibers and many stretched synthetic high polymers) constitute a special case. These are sometimes described as "pseudo uniaxial." The individual crystallites, or local oriented regions, are biaxial and within these the \mathbf{P} vectors are not symmetry fixed. If the crystallites are large compared to the unit cell dimensions, then the model to be applied is an array of partially oriented biaxial crystals. For each individual crystallite (A_{\max}/A_{\min}) still depends on the relative orientation of the dielectric ellipsoid and the transition moment vector, the latter coinciding with the direction of maximum absorption only in special cases. The dichroic ratios $R_{\text{polymer}} = A_{\parallel}/A_{\perp}$ of the whole chain would thus depend on the orientation of local polarization axes with respect to the chain axes, the relation between polarization axes and \mathbf{P} vectors within the crystallites, and the randomness of the chains. Unambiguous data can be obtained for bands with \mathbf{P} parallel or perpendicular to the chain axes and $\phi = 0$.

In Table 1 a comparison of idealized and calculated transition moment directions for eight group-frequency modes of the studied sample is given. The calculated directions, referred to the c -axis, are given by $\psi + \phi'$ or $\psi - \phi'$, if (ϵ_x/ϵ_y) is assumed to be unity. The error introduced by this assumption is small if ϕ' is close to zero, i.e. for the majority of the measured bands. If ϕ' has an appreciable value, as for the 1695 and 1200 cm^{-1} fundamentals, it should be kept in mind that ϕ' is merely a function of the ratio of the principal absorption coefficients. Ω gives the ideal directions.

In the studied crystal the directions of five out of eight \mathbf{P} vectors associated with modes which could be called separable group vibrations were—within the stated approximations—found to be close to idealized directions based on bond angles and local symmetries, but this was not generally true. The CH_2 bending modes, frequently referred to as "internal CH_2 group vibrations," were among the exceptions, the discrepancy for the 1463 cm^{-1} mode being close to 90° , which exceeds any possible measurement error. The assignment of this mode appears to be sound, and ϕ' was very small. (The band is certainly associated with CH_2 groups as shown by deuteration [17]. An alternative assignment as a wagging mode might be considered, but seems unlikely in view of the very large number of related compounds exhibiting relatively strong CH_2 bending modes very close to 1465 cm^{-1} [24, 25]). Actually, the two infrared active CH_2 bending modes of adipic acid are internal group vibrations only in a rough sense, as evidenced by their frequency difference of 55 cm^{-1} . The CH_2 groups are located close to highly polar end-groups which give rise to strong bands belonging to the same (molecular) symmetry species, B_u^m for C_{2h} symmetry. (B_u^m , A_u^m refer to molecular symmetry). In related structures with longer hydrocarbon chains [25] and in long-chain hydrocarbons [26], CH_2 bending modes are polarized approximately perpendicularly to the hydrocarbon chains, i.e. their behavior is more ideal in this respect. The CH_2 bending frequencies of these related compounds are within $\pm 10 \text{ cm}^{-1}$ of the 1463 cm^{-1} mode of adipic acid. It appears that more information on systems

[25] H. SUSI, *J. Amer. Chem. Soc.* **81**, 1535 (1959).

[26] S. KRIMM, *J. Chem. Phys.* **22**, 567 (1954).

with known structure is needed before the extent of interdependence of transition moment directions of "characteristic group vibrations" can be evaluated. The situation could be somewhat analogous to group frequencies, where bond stretching vibrations sufficiently far from other modes with the same symmetry are closest to "separable." However, polarization characteristics (like intensities) appear more sensitive to some interactions than frequencies. Polarization of the two B_u^f branches of bands for which idealized transition moment directions are determined by the symmetry of the whole molecule (A_u^m CH₂ rock., A_u^m OH bend.) was close to expectation.

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